# Exam 2019 - Solution

## Problem 1 : Permeable reactive barrier (30 points)

Mass Cr(VI) = $50\ \text{kg}$

Target concentration of Cr(VI) = 5 ppb

$\rho_{wb} = 1.8 \frac{\text{g}}{\text{cm}^3}$ = 1800 $\frac{\text{kg}}{\text{cm}^3}$

$\text{k} = 12\ \text{m}$

$\text{r} = 10\ \text{m}$

a- Aquifer dry bulk density

The dry bulk density is expressed by $\rho_b = \frac{M_S}{V_T}$ and the wet bulk density (given in the data of the problem) is expressed by $\rho_{wb} = \frac{M_S + M_L}{V_T}$.

We need to calculate $M_S$, $M_L$, and $V_T$.

- $V_T = \pi r^2 \times h$ ; $V_T = \pi \times 100 \times 12$ ; $V_T = 3\,769.9\ \text{m}^3$.
- $M_T = M_S + M_L = \rho_{wb} \times V_T$ ;
  $M_T = 3769.9\ \text{m}^3 \times 1.8 \frac{\text{g}}{\text{cm}^3} \times 10^6 \frac{\text{cm}^3}{\text{m}^3} \times \frac{1\text{kg}}{1000\text{g}}$ ;
  $M_T = 6.79 \times 10^6\ \text{kg}$
- $M_L = V_L \times \rho_{water}$ ; $M_L = \varepsilon \times V_T \times \rho_{water}$ ;
  $M_L = 3769.9\ \text{m}^3 \times 0.35 \times 997 \frac{\text{kg}}{\text{m}^3}$;
  $M_L = 1.32 \times 10^6\ \text{kg}$
- Hence, $M_S = M_T - M_L$ ; $M_S = 5.47 \times 10^6\ \text{kg}$
- And, $\rho_b = \frac{M_S}{V_T}$, $\rho_b = 1450 \frac{\text{kg}}{\text{m}^3}$.

b- Concentration of Cr(VI) in aqueous phase (necessary to determine the parameters of the PRB)

$m_{i,tot} = m_{i,aq} + m_{i,s}$ ; $m_{i,tot} = C_{i,aq} \times V_L + C_{i,s} \times M_s$ ;

$m_{i,tot} = C_{i,aq} \times \varepsilon V_T + C_{i,s} \times M_s$ , and $K_D = \frac{C_{i,s}}{C_{i,aq}}$ ;

Hence, $C_{i,aq} = \frac{m_{i,tot}}{\varepsilon V_T + K_D M_s}$ ;

$$C_{i,aq} = \frac{50\ \text{kg}}{0.35 \times 3769.9\ \text{m}^3 + 5.47 \times 10^6\ \text{kg} \times 0.2 \frac{\text{mL}}{\text{g}} \times \frac{1000\text{g}}{1\text{kg}} \times \frac{1}{10^6} \times \frac{1\text{m}^3}{\text{mL}}}$$ ;

$$C_{i,aq} = 2.07 \times 10^{-2} \frac{\text{kg}}{\text{m}^3} \times \frac{\text{m}^3}{1000\text{L}} \times \frac{10^9\ \mu\text{g}}{1\text{kg}}$$ ;

$C_{i,aq} = 2.07 \times \frac{10^4\ \mu g}{L}$.

From $K_D = \frac{C_{i,s}}{C_{i,aq}}$, we have $C_{i,s} = 0.2 \frac{mL}{g_{soil}} \frac{1L\ water}{1000\ mL} \times 2.07 \times 10^4\ \frac{\mu g}{L} \frac{1}{10^6} \frac{g}{\mu g}$;

$C_{i,s} = 4.14 \times 10^{-9} \times \frac{g_{Cr}}{g_{soil}} \times \frac{10^6\ \mu g\ Cr}{g_{Cr}} \times \frac{1000 g_{soil}}{kg_{soil}}$; $C_{i,s} = 4.14\ \frac{\mu g_{Cr}}{kg_{soil}}$.

c- Design of the PRB barrier

- $t_{res} = \frac{-\frac{\ln C_f}{C_0}}{k}$; $t_{res} = \frac{-\frac{\ln 5}{20070}}{5h^{-1}}$ ; $t_{res} = 1.66$ h.

- Groundwater velocity :
  $\upsilon = \frac{K \times i}{\varepsilon_{PRB}}$; $\upsilon = \frac{1.2 \times 0.5\ m.d^{-1}}{0.5}$; $\upsilon = 1.2\ m.d^{-1} \times \frac{1\ d}{24\ h}$; $\upsilon = 0.05 \frac{m}{h}$.

- Thickness of the PRB wall:
  $b = t_{res} \times \upsilon \times 3.5$ with 3.5 the safety factor
  $b = t_{res} \times \upsilon \times 3.5$ ; $b = 1.66\ h \times 0.05 \frac{m}{h} \times 3.5$ ; $b = 0.29$ m.

- Total volume barrier
  $V_{barrier} = w \times h \times b$ ; $V_{barrier} = 20 \times 15 \times 0.3$ ; $V_{barrier} = 90 m^3$. The volume chosen for calculation is slightly larger than volume needed.

d- Mass ZVI needed

$M_{ZVI} = V_{barrier} \times \rho_{ZVI}$ ; with $\rho_{ZVI} = \frac{2.3g}{cm^3}$ (bulk density)

$M_{ZVI} = 90 m^3 \times 2.3 \frac{g}{cm^3} \times \frac{1kg}{1000g} \times 10^6 \frac{cm^3}{1m^3}$;

$M_{ZVI} = 207000$ kg ;

$M_{ZVI} = 207$ metric tons .

## Problem 2 : Air stripping(40 points)

Groundwater contaminated with TCE

$C_{in} = 2300 \frac{\mu g}{L}$

$C_{out} = 100 \frac{\mu g}{L}$

Use air stripping to treat the water => will produce contaminated air => air will be treated with GAC

### Part 1: air stripping

Tower under 10m

Ratio $\frac{Q_A}{Q_W} = ?$

- start by assuming a ratio – test if tower < 10m
- $Q_W = 30 \frac{L}{s}$

Air stripping tower:

- Diameter $= 0.8\, m$, hence $S = \pi r^2$, $S = 0.5 m^2$.
- $K'_H = 0.415$
- $\alpha = 0.5\,; n = 0.2$
- $M_W(TCE) = 131.4\ g/mol$

Overall strategy:

1) Calculate stripping factor R
2) Calculate number of transfer units NTU
3) Calculate height of transfer unit HTU
4) Calculate height of tower Z

1) Calculate R

$R = K'_H \times \frac{Q_A}{Q_W}$ .

Assuming $\frac{Q_A}{Q_W} = 10$ , $R = 4.15$.

2) Calculate NTU

$NTU = \frac{R}{R-1} \times ln\left(\frac{C_{in}/C_{out} \times (R-1)+1}{R}\right)$ ; $NTU = 3.79$.

3) Calculate HTU

We have $HTU = \frac{L_M}{M_{water} \times K_L a}$ , so in order to calculate this, we need to calculate $L_M$ and $K_L a$ .

- Calculate $L_M$

First, we calculate L with $L = \frac{Q_W \times \rho_L}{S}$ .

$L = \frac{0.03 m^3/s \times 998.2\ kg/m^3}{0.5 m^2}$ ; $L = 59.6\ \frac{kg}{m^2 s}$ .

Hence, $L_M = \frac{L}{M_{water}}$ ; $L_M = \frac{59.6\ kg/m^2 s}{18 g/mol \times \frac{1kg}{1000g}}$ ; $L_M = 3309.8 \frac{mol}{m^2.s}$.

- Calculate $K_L a$

To calculate $K_L a$ , we use the simplified equation $K_L a = D_L \times \left(\frac{305 \times L}{\mu_L}\right)^{1-n} \times \left(\frac{\mu_L}{\rho_L \times D_L}\right)^{0.5} (s^{-1})$ .

First we need $D_L$ : $D_L = \frac{5.06 \times 10^{-10} \times T}{\mu_L \times V_m^{0.6}}$

We assume there that T is room temperature, let's use $T = 298K$.

$D_L = \frac{5.06 \times 10^{-10} \times 298K}{1.002 \times 10^{-3} \frac{kg}{m.s} \times 256^{0.6} \times \frac{cm^3}{mol}}$ ; $D_L = 5.402 \times 10^{-6}\ m^2/s$ .

Thus, $K_L a = 0.05 \times 5.402 \times 10^{-10}\ m^2/s \times \left(\frac{305 \times 59.6 \frac{kg}{m^2.s}}{1.002 \times 10^{-3} \frac{kg}{m.s}}\right)^{0.8} \times \left(\frac{1.002 \times 10^{-3} \frac{kg}{m.s}}{998.2 \frac{kg}{m.s} \times 5.402 \times 10^{-10} m^2/s}\right)^{0.5}$ ;

$K_L a = 0{,}00746\ s^{-1}$.

We can then calculate HTU:

$HTU = \frac{L_M}{M_{water} \times K_L a}$ ; $HTU = \frac{3309.8 \frac{mol}{m^2.s}}{\frac{55.600 mol}{m^3} * 0.0186}$ ; $HTU = 8$ m.

4) Calculate Z

Eventually, $Z = HTU \times NTU$; $Z = 30$ m.

This is Ok, so we can extract $Q_A = 0.3 \frac{m^3}{s} = 300\ L/s$.

## Part 2: GAC

To design the GAC we need to know:

- How many drums?
- How to arrange?
- How long it will take to exhaust the barrels?

We have:

- $Q_A = 300\ L/s$
- Height 2,5m
- Diameter 0.7 m
- Cross section: $S = \pi r^2$ ; $S = 0.38\ m^2$.
- $\Gamma = 475 \times C^{0.83}$

1) Adsorption capacity of GAC

First we need to calculate the concentration in the gas when it enters the GAC.

In an air stripping tower, the gas outlet is in equilibrium with the water inlet:

$C_{G,GAC} = K_H C_{L,in} = 0.415 \times 2{,}300 \frac{\mu g}{L} = 954.5 \frac{\mu g}{L}$

$\Gamma = 475 \times C^{0.83}$ ; $\Gamma = 475 \times \left(\frac{0.955 mg}{L}\right)^{0.83}$ ; $\Gamma = 457 \frac{mg\ TCE}{g\ GAC}$

If we assume an efficiency of 50%, the adsorption capacity is then:

$\Gamma_{50\%} = 229 \frac{mg\ TCE}{g\ GAC}$

2) Amount of activated carbon per drum $M_{AC}$

$M_{AC} = V_{barrel} \times \rho_{AC}$ ; $M_{AC} = h\pi r^2 \times \rho_{AC}$; $M_{AC} = 0.96 \times 500 \frac{kg}{m^3}$ ; $M_{AC} = 481 kg$.

3) TCE retained per drum $M_{TCE,retained}$

$M_{TCE,retained} = 481 \frac{kg\ GAC}{drum} \times 229 \frac{mg\ TCE}{g\ GAC} \times \frac{1000 g}{1 kg} \times \frac{1 \text{kg}}{10^6 mg}$ ;

$M_{TCE,retained} = 110 \frac{kg\ TCE}{drum}$ .

4) Assumptions for the design

$EBCT = 12 min$

$SLR = 150 \frac{L}{s.m^2}$

5) Design

- $V_{AC} = 300 \frac{L}{s} \times 5 min \times 60 \frac{s}{min}$ ; $V_{GAC} = 216\,000 L$ ; $V_{GAC} = 216\ m^3$.
- Cross section area: $A_{AC} = \frac{Q}{SLR}$ ; $A_{AC} = \frac{300 \frac{L}{s}}{150 \frac{L}{s.m^2}}$ ; $A_{AC} = 2\ m^2$.

  So we need 6 drums in parallel.
- Height needed: $H_{AC} = \frac{V_{AC}}{A_{AC}}$ ; $H_{AC} = 108\ m$ .

  We need 44 drums in series

  In total, $6 \times 44 = 264\ drums$.

6) Mass removal rate $Rremoval$

$Rremoval = Q \times C$ ; $Rremoval = 300 \frac{L}{s} \times 0.955 \frac{mg}{L}$ ; $Rremoval = 286.5 \frac{mg}{s}$ ;

If we change the units to $kg/day$ :

$Rremoval = 286.5 \frac{mg}{s} \times \frac{86400 s}{day} \times \frac{1 kg}{10^6 mg}$ ; $Rremoval = 24.75 \frac{kg}{day}$ .

7) Time until exhaustion

Each drum hold $110\ kg\ TCE$, and we have 264 drums so $29{,}079\ kg\ TCE$ can be hold in total.

So $\frac{29{,}079 kg}{24.75 kg/day} = 1{,}175\ days$ until exhaustion.

## Problem 3 : Chemical oxidation (30 points)

1) How many batches of soil land farming?
2) How much persulfate needed?
3) How much time to degrade TCA below 50mg/kg?

1) <u>Number of batches</u> $N_{batches}$

The volume of each batch is $V_{batch} = 40 \times 25 \times 0.3$ ; $V_{batch} = 300 m^3$.
The total volume of soil excavated is $7000 m^3$.
So $N_{batches} = \frac{7000\ m^3}{V_{batch}}$, $N_{batches} = 24$ batches.

2) How much persulfate needed?

Need to calculate:

- Concentrations in solution and solid phase before treatment
- Concentrations in solution and solid phase after treatment (target)
- The quantity of TCA to remove
- Stoichiometry of the reaction
- Total persulfate needed $m_{sodium-persulfate}$

- Concentrations before treatment:

$m_{TCA,tot} = V_{TCA} \times \rho_{TCA}$; $m_{TCA,tot} = 10 m^3 \times 1325 \frac{kg}{m^3}$ ; $m_{TCA,tot} = 13250\ kg$.

And $m_{TCA,tot} = m_{TCA,aq} + m_{TCA,s} + m_{TCA,g}$ ;
$m_{TCA,tot} = C_{TCA,aq} \times (V_L + K_D M_s + K'_H V_G)$ ;
Hence, $C_{TCA,aq} = \frac{m_{TCA,tot}}{(V_L + K_D M_s + K'_H V_G)}$ .

To determine $V_G$ and $V_L$, we have $V_T = 7000\ m^3$, and $V_G + V_L = \varepsilon V_T$.
Also $V_L = \theta V_T$, with $\theta$ the moisture content.
So $V_L = 0.1 \frac{m^3}{m^3} \times 7000\ m^3$; $V_L = 700\ m^3$.
$V_G + V_L = 1750\ m^3$ .
Hence $V_G = 1050\ m^3$ .

Then to find $M_S$ :
$M_T = M_s + M_L$ ; $M_s = M_T - \rho_L V_L$ .
and $M_T = \rho_{wb} \times V_T$, hence $M_T = 1800 \frac{kg}{m^3} \times 7000\ m^3$ , $M_T = 1.26 \times 10^7\ kg$ .
Then, $M_s = 1.19 \times 10^7\ kg$ .

We can then calculate $C_{TCA,aq} = \frac{m_{TCA,tot}}{(V_L + K_D M_s + K'_H V_G)}$ ;

$C_{TCA,aq} = \frac{13250\ kg}{700 m^3 + 10^{-2} \frac{m^3}{kg} \times 1.09 \times 10^7 kg + 0.56 \times 1050 m^3}$ ; $C_{TCA,aq} = 0.11 \frac{kg}{m^3}$ .

$C_{TCA,s} = K_D \times C_{TCA,aq}$ ; $C_{TCA,s} = 10^{-2} \frac{m^3}{kg_{soil}} \times 0.11 \frac{kg_{TCA}}{m^3}$

$C_{TCA,s} = 1.1 \times 10^{-3} \frac{kg_{TCA}}{kg_{soil}} = 1.1 \frac{g_{TCA}}{kg_{soil}}$ ;

Concentrations after treatment:

$C_{TCA,target,s} = 50 \frac{mg_{TCA}}{kg_{soil}}$

$C_{TCA,target,aq} = \frac{C_{TCA,target,aq}}{K_D}$ ; $C_{TCA,target,aq} = \frac{50 \frac{mg_{TCA}}{kg_{soil}}}{10^{-5} \frac{m^3_{water}}{g_{soil}}}$ ; $C_{TCA,target,aq} = 0.005 \frac{kg_{TCA}}{m^3_{water}}$.

- The quantity of TCA to remove is:

$$m_{TCA,to\ remove} = M_S\left(C_{TCA,initial,S} - C_{TCA,target,S}\right) + V_L\left(C_{TCA,initial,aq} - C_{TCA,target,aq}\right)$$
$$= 1.19 \times 10^7\ kg \times \left(1.1 - 50 \times 10^{-3} \frac{g_{TCA}}{kg_{soil}}\right) + 700\ m^3 \times \left(110 - 5 \frac{g_{TCA}}{m^3_{water}}\right) = 12{,}569\ kg_{TCA}$$

- Stoichiometry of the oxidation reaction¨

$$4 \times (S_2O_8{}^{2-} + e^- \rightarrow 2SO_4{}^{2-})$$
$$C_2H_3Cl_3 + 4H_2O \rightarrow 2CO_2 + 3Cl^- + 8e^- + 11H^+$$

need 4 moles of persulfate per moles of TCA

- Total persulfate needed $m_{sodium-persulfate}$

$m_{sodium-persulfate} = \frac{m_{TCA\ to\ remove}}{M_w(TCA)} \times M_w(Na_2S_2O_8) \times 4$ ;

$m_{sodium-persulfate} = \frac{12{,}569kg}{133.4 \frac{g}{mol}} \times 238 \frac{g}{mol} \times 4$;

$m_{sodium-persulfate} = 89{,}698\ kg$ .

3) <u>Time to degrade TCA</u>

For one batch:

$C = C_0 e^{-kt}$ , with $k = 0.1\ d^{-1}$ .

$-\frac{1}{k} \ln\left(\frac{C}{C_0}\right) = t$ , then $t = -\frac{1}{0.1} \times \ln\left(\frac{0.005}{0.11}\right)$ , $t = 30.9\ days\ per\ batch$ .

Total time:

$t_{tot} = 742\ days$ .